

Computer simulation of polydioxolane (PDXL) and poly(tetrahydrofuran) (PTHF): a comparative study of some poly(ethylene oxide) (PEO) properties

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Abstract

Classical methods (molecular mechanics and molecular dynamics) and semiempirical calculations were applied to study structural and energetic properties of polydioxolane (PDXL) and poly(tetrahydrofuran) (PTHF). Then, these properties were compared with poly(ethylene oxide) (PEO) in order to investigate the possibility of using PDXL and PTHF as an alternative to PEO based systems. It was found that the behaviour of molecular simulation is similar for all of them, with the folded structure observed in equilibrium. It was noted that the main contribution to potential energy is due to electrostatic term. The O/C ratio and oxygen atom positions have a strong influence on charge distribution. Semiempirical calculations of free energy including enthalpic, entropic and zero point energy (ZPE) contributions showed that the folding process is favourable for PEO, PTHF and PDXL at 300 and 400 K. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyethers are typical polymers where the presence of electron-rich oxygen atom in the backbone structure offers a precious site of coordination. Besides, these systems have the ability of electron-poor groups to associate with these polymers, an important characteristic for their use in many ways [1–3]. In this context, low molecular weight polymers (molecular weight of

200–20 000) are used in ceramics, cosmetics, lubricants, metalworking, pharmaceuticals, rubber chemical, electronics and other applications [4].

One of the most widely studied polyether is poly(ethylene oxide) (PEO), where the presence of an oxygen atom in every third position of the backbone produces a standard system exhibiting a significant impact on physical and chemical properties. The application of PEO is mainly salts dissolution without the addition of any solvent aimed at the construction of polymer electrolyte materials [5–11].

The advances in the techniques used to construct and analyse chemically complex molecules and also on the computational modelling of molecules or set of molecules has become an important tool for designing

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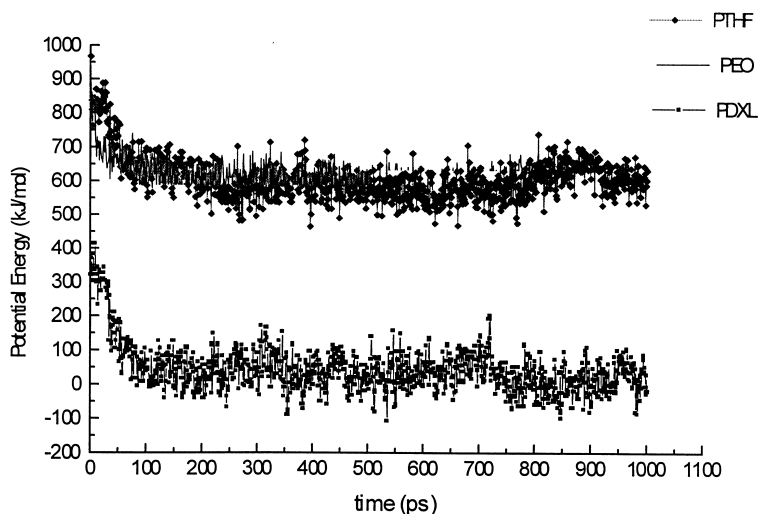


Fig. 1. Potential energy (kJ/mol) as a function of time (ps) for PTHF (light grey), PEO and PDXL, containing 20 monomeric units at 300 K in vacuum.

new compounds and investigation of their properties. In this sense, an initial investigation is proposed based on a theoretical study of alternative polyethers which a priori could exhibit similar properties as PEO [12–14]. Thus, poly(1,3-dioxolane) and poly(tetrahydrofuran) (PTHF) containing 20 monomeric units are studied in order to verify the effects of position of oxygen atoms and the O/C ratio (number of oxygen atoms divided by the number of carbon atoms in each monomeric unit) of suitable analogous in some parameters and produce properties to be compared with PEO ones.

2. Theory and methods

Molecular mechanics and molecular dynamics simulations were used in the present calculations. At a heart of such theoretical calculations are empirical force fields, which describe the interatomic interactions and the mechanics of deformations of the molecules. These calculations can be done by the laws of classical physics (Newton's laws), and a potential energy functions are used [15].

Typically, the energy of a molecule is calculated as a sum of the steric and presence of non-bonded inter-

actions. Therefore, each bond length, angle and dihedral is treated individually while non-bonded interactions represent the influence of non-covalent forces [16]:

$$E_{\text{total}} = E_l + E_\theta + E_w + E_{\text{nb}} \quad (1)$$

where E_l , E_θ , E_w and E_{nb} are, respectively, bond length, angle, dihedral and non-bonded energies. The first three terms can be grouped as the bonded interactions. The non-bonded interactions (E_{nb}) are calculated as a sum over all the atoms with a 1–4 or greater separation. It is usual to consider these interactions as having two components: electrostatic (E_{el}) and van der Waals (E_{vdW}). The electrostatic term is expressed by

$$E_{\text{el}} = \sum q_i q_j / D r_{ij} \quad (2)$$

and the most common van der Waals interaction is the Lennard-Jones potential:

$$E_{\text{vdW}} = \sum \epsilon [(r_m/r)^{12} - 2(r_m/r)^6] \quad (3)$$

The four terms in Eq. (1) constitute the core of almost all molecular mechanics force field; in some cases, however, it is necessary for additional terms to be included, as hydrogen bond energy and cross terms

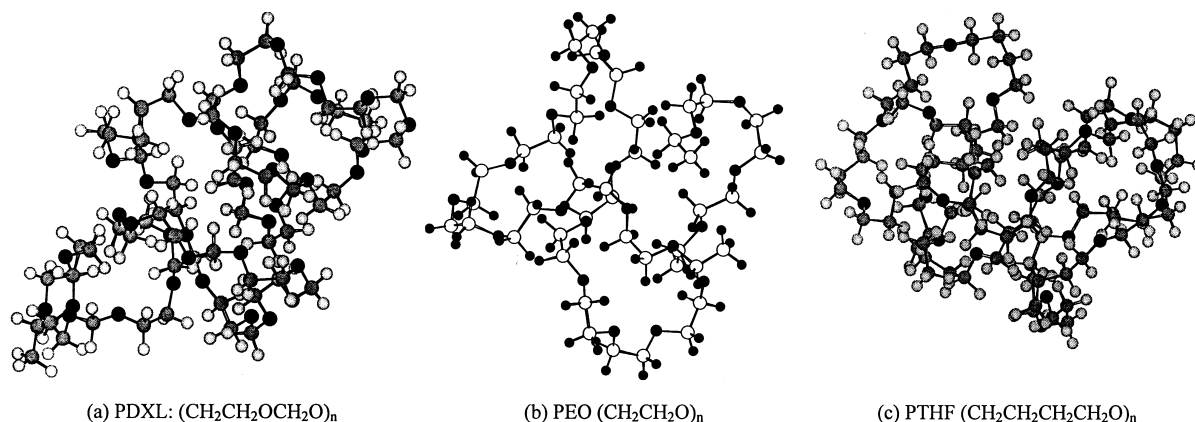


Fig. 2. Equilibrium structures obtained for (a) PDXL; (b) PEO; and (c) PTHF containing 20 monomeric units at 300 K in vacuum after 1000 ps of Molecular Dynamics simulations.

(bend–bend, torsion–bend, etc.). A good review on this subject is given in Ref. [17].

In a recent paper [18], classical methods (molecular mechanics and molecular dynamics (MDM)) were applied to investigate the PEO behaviour. In the present simulations a similar study was performed in order to compare energetic and structural behaviour between PEO– $(\text{CH}_2\text{CH}_2\text{O})_n$ –, PDXL– $(\text{CH}_2\text{CH}_2\text{OCH}_2\text{O})_n$ – and PTHF– $(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n$ – containing 20 monomeric units. The optimised potentials for liquid simulations (OPLS) force field [19] implemented in Macromodel program [20] was used.

The systems were simulated at a fixed temperature (300 and 400 K) in vacuum during a total time of $t = 1000$ ps and the time step was $\Delta t = 1$ fs using a minimised linear structure as initial point. These simulations were performed on a Silicon Graphics R-10000 workstation.

Enthalpic, entropic and zero point energy (ZPE) contributions for the folding process of these polyethers at 300 and 400 K were obtained by using the semiempirical method AM1 (Austin Model 1) implemented in the MOPAC93.00 version 7.0 program [21,22]. The initial linear and final folded (equilibrium state) structures obtained from the MDM simulations were fully optimised before the thermodynamical properties calculations. The following keywords were used: AM1, precise, ef, ddmin = 0.0, grad, geo-ok, gnorm = 0.5. The calculations of the thermodynamical properties were performed using the statistical thermodynamics formalism (keywords force and thermo). The meaning of the cited keywords is specified in the MOPAC manual [22]. The AM1 calculations were performed on a Sun Ultra 1 workstation.

3. Results and discussion

The evolution of the total potential energy as a function of time at 300 K is shown in Fig. 1. At 400 K, behaviour of the systems is similar. As we can observe, after 400 ps, the systems reached the equilibrium state. The equilibrium structures obtained at 1000 ps of simulation at 300 K in a vacuum for PEO, PDXL and PTHF containing 20 monomeric units are shown in Fig. 2. It can be noted that the simulations led to folded structures at the equilibrium

Table 1

Values of kinetic (K), potential (V) and total energies in vacuum at 300 and 400 K for PDXL, PEO and PTHF

Energy (kJ/mol)	300 K			400 K		
	PDXL	PEO	PTHF	PDXL	PEO	PTHF
K	834	546	972	1111	728	1304
V	48	611	610	396	833	1008
Total energy ^a	882	1157	1582	1506	1561	2312

^a Standard deviation: ~2%.

Table 2

Values of all contributions for potential energy in vacuum at 300 and 400 K for PDXL, PEO and PTHF

Energy (kJ/mol)		300 K			400 K		
		PDXL	PEO	PTHF	PDXL	PEO	PTHF
V	Stretching	294	191	332	388	258	443
	Bending	461	296	532	597	392	691
	Torsion	185	118	149	204	137	190
	vdW	−190	−103	−168	−135	−64	−83
	Electrostatic	−702	109	−235	−658	110	−233
	Total V	48	611	610	396	833	1008

state for all polyethers studied. Table 1 presents the values of kinetic, potential and total energies. Table 2 summarises all contributions for potential energy. PEO was included in both tables for reason of comparison.

The different results for kinetic values are due to different species number (atoms) in each monomeric unit of PEO, PDXL and PTHF: $K_{\text{PTHF}} > K_{\text{PDXL}} > K_{\text{PEO}}$. It can be observed that the van der Waals contribution (E_{vdW}) has a negative value for all of the polyethers — an attractive potential — which confirms that the van der Waals term is an important contribution to the folding process for these molecules. On the other hand, it is interesting to note that the electrostatic contribution (E_{el}) shows a different behaviour: for PEO we obtained a repulsive potential (positive value of E_{el}) and for PDXL and PTHF, we obtained an attractive potential (negative values of E_{el}). This can be explained by using the influence of

oxygen atom positions and O/C ratio on the backbone charge distribution. As we have pointed out before (Section 2), the electrostatic contribution is due to the non-bonded interactions: 1–4 interactions and greater separation. From Fig. 3 it is clear that the number and position of oxygen atoms are closely related to the observed values of those interactions. In the case of PEO, all non-bonded interactions are repulsive (positive–positive and negative–negative interactions) and it leads to positive values of the electrostatic potential ($E_{\text{el}} = 109$ kJ/mol at 300 K and $E_{\text{el}} = 110$ kJ/mol at 400 K). If a similar analysis is performed to PDXL and PTHF, we can observe that in both cases, the interactions lead to negative values of electrostatic potentials, but these interactions are more expressive for the PDXL system than PTHF (Table 2). Such observation is based on the fact that in PTHF system almost all the interactions are neutral: it happens between null-positive or null-negative charges. It leads to a smaller value of electrostatic potential than that of PDXL system.

The end-to-end carbon distances (Fig. 4) and the average of gyration radii (Table 3) were calculated at 300 and 400 K for PDXL, PEO and PTHF by picking up six configurations at $t = 500, 600, 700, 800, 900$ and 1000 ps that represents the equilibrium state. These results exhibit the same tendency of folding structures in the equilibrium state, in agreement with Fig. 2. The average of gyration radii of these molecules has very close values at 300 K and these values increase slightly at 400 K. It is interesting to observe that at 400 K the deviation is larger than at 300 K. Besides, it is interesting to note that — for PDXL molecule — the larger value of the O/C ratio and the different oxygen atoms position lead to a larger electrostatic contribution, producing a smaller

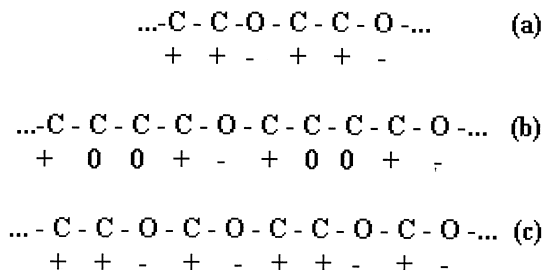


Fig. 3. Schematic charge distribution for the backbone chain for (a) PEO; (b) PTHF; and (c) PDXL. The signs represent the net charges values of each atom, obtained from the Molecular Dynamics simulations in vacuum at 300 K. The typical values are +0.245 for positive charges and −0.406 for negative charges (both end atoms and hydrogens were not included, but its charge distributions lead to electroneutral systems).

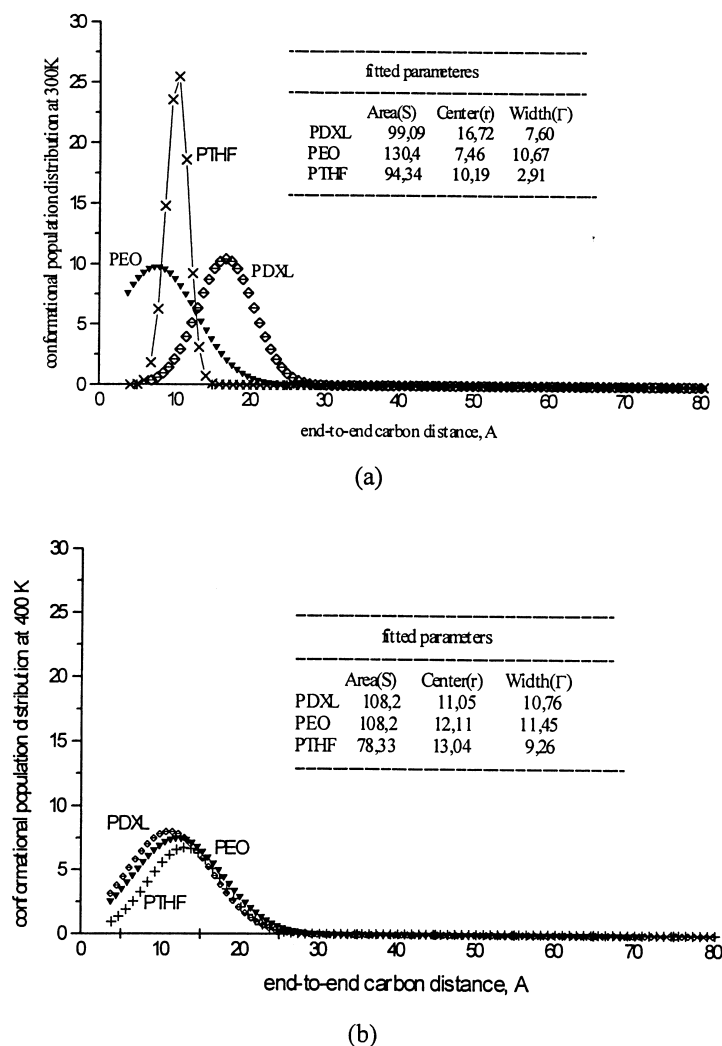


Fig. 4. Gaussian fit to conformational population distribution as function of end-to-end carbon distance at (a) 300 and (b) 400 K for PDXL, PEO and PTHF.

Table 3

Average gyration radii for PDXL, PEO and PTHF at 300 and 400 K. The average was obtained by using the gyration radii of configurations at $t = 500, 600, 700, 800, 900$ and 1000 ps

T (K)	Average gyration radii (Å)		
	PDXL	PEO	PTHF
300	6.6(4)	5.5(2)	7.0(2)
400	6.9(2)	6.0(5)	7.7(8)

deviation on the gyration radii values when the temperature is increased from 300 to 400 K.

The conformational population distribution as a function of the end-to-end carbon distances show that PDXL, PEO and PTHF have approximately the same centre (r) values at 400 K. However, the centre values at 300 K can be reported as $r_{\text{PDXL}} (16.7 \text{ Å}) > r_{\text{PTHF}} (10.2 \text{ Å}) > r_{\text{PEO}} (7.45 \text{ Å})$. It means that certainly both O/C ratio and the oxygen atoms position of PEO confirm that this system is a standard structure and modification of these parameters can a

Table 4

Thermodynamic properties (kcal/mol) for the folding process in PDXL, PEO and PTHF molecules in a vacuum at 300 and 400 K calculated using the AM1 method

	ΔH_T^0 ^a	$-T\Delta S_T^0$ ^b	ΔZPE ^c	ΔG_T^0 ^d
300 K				
PDXL	-36.18	26.4	-1.742	-11.52
PEO	-17.28	-15.3	5.929	-26.65
PTHF	5.897	2.4	-10.17	-1.87
400 K				
PDXL	-7.898	9.2	-8.682	-7.38
PEO	-14.96	-28.4	6.731	-36.63
PTHF	-0.373	10.4	-37.85	-27.82

^a $\Delta H_T^0 = \Delta H_{f,T}^0(\text{folded}) - \Delta H_{f,T}^0(\text{linear})$, where $\Delta H_{f,T}^0$ is the heat of formation calculated at the temperature T .

^b $\Delta S_T^0 = S_T^0(\text{folded}) - S_T^0(\text{linear})$.

^c $\Delta ZPE = ZPE(\text{folded}) - ZPE(\text{linear})$, where ZPE is the zero point energy.

^d $\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 + \Delta ZPE$.

priori produce a different kind of folding process at room temperatures. In spite of such observation, the system based in PEO, PDXL and PTHF will probably have the same structural behaviour at both temperatures.

The MDM calculations considered only the enthalpic contribution to the folding process analysis. Thus, semiempirical AM1 calculations were performed in order to calculate the entropic and ZPE contributions and the free energy. Calculations of the thermodynamic properties were performed using AM1 fully optimised geometries obtained from the simulations. We considered the initial and the equilibrium structures of PDXL, PEO and PTHF at 300 and 400 K. The results are shown in Table 4. From these results we can conclude that the contribution from the entropic variation is not relevant to the folding process. If the $-T\Delta S$ term at 300 and 400 K is considered to this analysis, it could be shown that its contribution is quite important to the free energy calculations: for PEO, the $-T\Delta S$ term lead to favourable ΔG values for the folding process, and for both PTHF and PDXL the $-T\Delta S$ term lead to ΔG values which is not favouring the folding process. Despite the fact that the entropic contribution is not favouring the folding process, it could be noted that the ΔZPE contribution — included on the ΔG calculations — is an important contribution to the folding process: ΔG values (including the three contributions)

are negative and it means that the process is still favourable for these molecules, but less favourable than PEO at both temperatures. All molecules have the same behaviour (a folded structure at 300 and 400 K) and the gyration radii are slightly increased at 400 K.

4. Conclusions

Classical and quantum mechanical semiempirical methods were applied in order to compare some properties of polyethers containing 20 monomeric units with a different O/C relation at 300 and 400 K in vacuum. Comparisons were made for PDXL and PTHF with PEO, the final a standard system for many applications. From the MDM results, we can conclude that PDXL, PEO and PTHF simulations lead to folded structures at the equilibrium, which can be confirmed by the end-to-end carbon distance as a function of conformational population distribution and the radii of gyration values. The centre values (r) showed that PDXL, PEO and PTHF at 300 K certainly suffer either an influence of both O/C ratio and of the oxygen atoms position. These parameters can a priori produce a different kind of folding process at room temperatures. At 400 K, the centre values are approximately the same. The main contributions to the potential energy are the electrostatic and van der Waals terms, the first being more important than the second one. Moreover, it means that the O/C ratio and oxygen atoms position is relevant to the charge distribution, the electrostatic contribution (non-bonded interactions) and to the attractive/repulsive potentials. From the AM1 calculations, we can conclude that the both entropic ($-T\Delta S$ term) and ZPE contributions are relevant to the free energy variation for the folding process and this process is favourable at temperatures of 300 and 400 K.

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